

Crosslinked cationic copolymers with regulators and their use in hair cosmetic preparations

5 The present invention relates to the use of polymers obtainable by free-radically initiated copolymerization of monomer mixtures of

- (a) at least one cationic monomer or quaternizable monomer
- 10 (b) optionally a water-soluble monomer,
- (c) optionally a further free-radically copolymerizable monomer
- (d) at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds, and
- (e) at least one regulator

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and subsequent quaternization or protonation of the polymer if the monomer (a) used is a nonquaternized polymer or an only partially quaternized monomer, as active ingredients in cosmetic preparations, in hair cosmetic preparations, and to the use of

20 these polymers as conditioning agents in cosmetic preparations.

Cationic polymers are used as conditioning agents in cosmetic formulations. Requirements for hair conditioning agents are, for example, a considerable reduction in the required combing force

25 in wet and also dry hair, good detangling on the first combing and good compatibility with other formulation components. In addition, cationic polymers prevent electrostatic charging of the hair.

30 In shampoos, cationic cellulose derivatives (polyquaternium-10) or guar gum derivatives are primarily used. However, a build-up effect is observed with these compounds, i.e. the hair becomes coated with the conditioner with repeated application and feels weighted down.

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For the conditioning and setting of keratin substances, such as hair, nails and skin, synthetic polymers have also been used for years. In addition, synthetic polymers are used in cosmetic formulations which comprise pigments or cosmetically effective

40 active components as compatibility promoters for achieving a homogeneous, stable formulation.

For example, copolymers of acrylamide and dimethyldiallylammonium chloride (polyquaternium 7) are used. However, these have the

45 disadvantage of high residual monomer contents since acrylamide

and dimethyldiallylammonium chloride have unfavorable copolymerization parameters.

Despite extensive efforts, there is still a need for improvement
5 in the case of polymers for generating elastic hairstyles with simultaneously strong hold even at high atmospheric humidity, good ability to be washed out and good feel of the hair. The need for improvement likewise consists in the case of polymers for generating readily combable, detanglable hair and for the
10 conditioning of skin and hair in their sensorially perceptible properties, such as feel, volume, handlability etc. Also desirable are clear aqueous preparations of these polymers which are characterized, accordingly, by good compatibility with other formulation constituents.

15 In addition, there is a need for polymers which are suitable as conditioning agents for cosmetic preparations and which can be prepared with a high solids content. Of particular interest are polymers which have a high solids content, have a low viscosity
20 with simultaneously good performance properties (such as, for example, combability).

It is an object of the present invention to find a cationic conditioning agent for cosmetic preparations, in particular
25 shampoos, which does not have said disadvantages.

Quaternized polymers and their use as conditioning agents in hair care formulations are known.

30 Cationic polymers are often used as conditioning agents in hair cosmetic formulations. They bring about primarily an improvement in the wet combability of hair. In addition, cationic polymers prevent electrostatic charging of hair.

35 Thus, for example, EP-A-0 246 580 describes the use of noncrosslinked homo- and copolymers of 3-methyl-1-vinylimidazolium chlorides in cosmetic compositions. EP-A-0 544 158 and US-A-4,859,756 claim the use of noncrosslinked homo- and copolymers of chloride-free, quaternized
40 N-vinylimidazoles in cosmetic preparations. EP-A-0 715 843 discloses the use of noncrosslinked copolymers of a quaternized N-vinylimidazole, N-vinylcaprolactam and N-vinylpyrrolidone, and optionally a further comonomer in cosmetic preparations.

45 DE-A-28 21 239 (US-A-4,348,380) and DE-A-31 06 974 describe copolymers of quaternized diallylammonium compounds in hair cosmetic preparations.

US-A-5,275,809, EP-A-0 522 755, EP-A-0 521 665 and EP-A-0 521 666 disclose copolymers with dimethyldiallylammonium chloride for use in shampoos. None of the abovementioned specifications describes a crosslinked polymer.

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In addition, crosslinked cationic copolymers and their use as water-soluble and water-insoluble additives in very diverse fields are also described.

US-A-4,806,345 describes crosslinked cationic thickeners for
10 cosmetic formulations of quaternized dimethylaminoethyl methacrylate and acrylamide.

WO 93/25595 describes crosslinked cationic copolymers based on quaternized dialkylaminoalkyl acrylates or
15 dialkylaminoalkylacrylamides. As an application, the use of these crosslinked copolymers as thickeners in cosmetic preparations is proposed. These polymers do not comprise regulators.

DE 3 209 224 describes the preparation of crosslinked polymers
20 based on N-vinylpyrrolidone and (quaternized) N-vinylimidazole. These polymers are claimed for use as adsorbents and ion exchangers. They are highly crosslinked, water-insoluble, sparingly swellable and therefore not suitable as conditioning agents in cosmetic formulations.

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Crosslinked agglomerated vinylimidazole copolymers are mentioned in WO 96/26229 as dye transfer inhibitors. They are highly crosslinked, water-insoluble, not very swellable and are therefore not suitable as conditioning agents in cosmetic
30 formulations.

US-A-4,058,491 discloses crosslinked cationic hydrogels of N-vinylimidazole or N-vinylpyrrolidone and a quaternized basic acrylate and other comonomers. These gels are proposed for the
35 complexing and controlled release of anionic active substances.

DE-A-42 13 971 describes copolymers of an unsaturated carboxylic acid, quaternized vinylimidazole and optionally further monomers and a crosslinker. The polymers are proposed as thickeners and
40 dispersants.

The method of thickening by protonating a water-soluble, crosslinked aminoalkyl (meth)acrylate is described in EP-A-0 624 617 and EP-A-0 027 850.

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WO 96/37525 describes the preparation of crosslinked copolymers from, inter alia, N-vinylpyrrolidone and quaternized vinylimidazoles in the presence of polymerization regulators and their use, in particular, in detergents.

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WO 97/35544 describes the use of crosslinked cationic polymers with dialkylaminoalkyl (meth)acrylates or dialkylaminoalkyl (meth)acrylamides in shampoo compositions.

10 DE-A-197 31 907 describes the use of crosslinked cationic copolymers which contain N-vinylimidazoles in hair cosmetic formulations.

EP 0 893 117 and EP 1 064 924 describe high molecular weight
15 crosslinked polymers which have a good conditioning effect in shampoos, while the corresponding low molecular weight noncrosslinked polymers exhibit only low effectiveness as conditioning agents.

20 A disadvantage of these abovementioned inventions is that the preparation of these polymers as solutions takes place with a very low solids content because otherwise the viscosities of these solutions are too high. An additional disadvantage is the production of a relatively large fraction of undissolved gel
25 particles. This leads to a large number of performance disadvantages, such as, for example, prolonged polymerization times, and long filtration and bottling times. The low solids content results in high costs during the preparation (vessel capacities) and high transportation costs.

30

It is an object of the present invention to provide polymers which are suitable for cosmetic preparations, in particular hair cosmetic preparations (conditioning properties), have a satisfactory viscosity and can also be prepared with a high
35 solids content. Of particular interest are polymers which comprise fewer gel particles than the polymers of the prior art, in particular of EP 0 893 117.

We have found that this object is achieved by the polymers
40 according to the invention.

The use according to the invention relates to polymers obtainable by

45 (i) free-radically initiated copolymerization of monomer mixtures of

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- (a) at least one cationic monomer or quaternizable monomer
 - (b) optionally a water-soluble monomer,
 - (c) optionally a further free-radically copolymerizable monomer
 - 5 (d) at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds, and
 - (e) at least one regulator
- 10 (ii) subsequent quaternization or protonation of the polymer if the monomer (a) used is a nonquaternized monomer or is an only partially quaternized monomer.

The use according to the invention relates to polymers obtainable
15 by (i) free-radically initiated copolymerization of monomer mixtures of

- (a) 1 to 99.98% by weight, preferably 2 to 70% by weight, particularly preferably 2 to 50% by weight, of at least one
20 cationic monomer or quaternizable monomer
- (b) 0 to 98.98% by weight, preferably 22 to 97.98% by weight, particularly preferably 45 to 85% by weight, of at least one water-soluble monomer,
- 25 (c) 0 to 50% by weight, preferably 0 to 40% by weight, particularly preferably 0 to 30% by weight, of a further free-radically copolymerizable monomer,
- 30 (d) 0.01 to 10% by weight, preferably 0.02 to 8% by weight, particularly preferably 0.05 to 5% by weight, of at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds, and
- 35 (e) 0.01 to 10% by weight, preferably 0.02 to 8% by weight, particularly preferably 0.05 to 5% by weight, of a regulator

and (ii) subsequent quaternization or protonation of the polymer if the monomer (a) used is a nonquaternized monomer or an only
40 partially quaternized monomer, as conditioning agent for compositions in hair cosmetics.

The polymers obtainable in this way are suitable for use in hair cosmetic preparations.

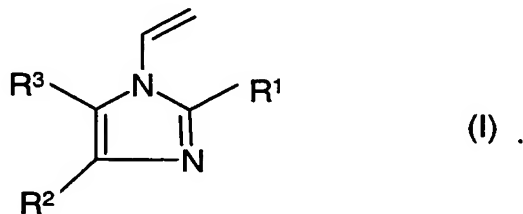
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The polymers obtainable in this way are suitable as conditioning agents in cosmetic preparations, in particular in skin and/or hair cosmetic preparations.

5 Preference is given to the use in shampoos.

Suitable monomers (a) are the N-vinylimidazole derivatives of the formula (I) in which R¹ to R³ are hydrogen, C₁-C₄-alkyl or phenyl

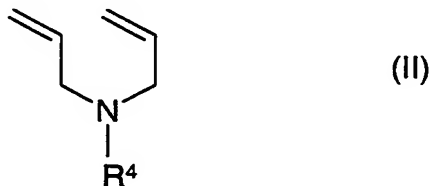
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Also suitable are diallylamines of the formula (II) in which R⁴ is C₁-C₂₄-alkyl

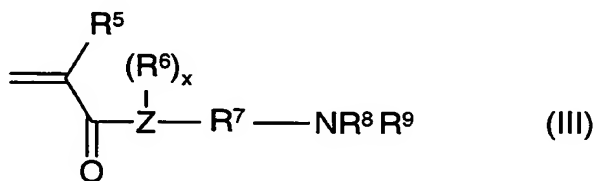
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Also suitable are N,N-dialkylaminoalkylacrylates and methacrylates and N,N-dialkylaminoalkylacrylamides and -methacrylamides of the formula (III),

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where R⁵, R⁶ independently, are a hydrogen atom or a methyl radical, R⁷ is an alkylene radical having 1 to 24 carbon atoms, optionally substituted by alkyl radicals, and R⁸, R⁹ are C₁-C₂₄ alkyl radicals. Z is a nitrogen atom together with x = 1 or an
 40 oxygen atom together with x = 0.

Examples of compounds of the formula (I) are given in Table 1 below:

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Table 1

	R ¹	R ²	R ³
5	H	H	H
	Me	H	H
	H	Me	H
	H	H	Me
	Me	Me	H
10	H	Me	Me
	Me	H	Me
	Ph	H	H
	H	Ph	H
	H	H	Ph
15	Ph	Me	H
	Ph	H	Me
	Me	Ph	H
	H	Ph	Me
	H	Me	Ph
	Me	H	Ph

20 Me = methyl

Ph = phenyl

Other monomers of the formula (I) which can be used are the ethyl, propyl or butyl analogs of the methyl-substituted

25 1-vinylimidazoles listed in Table 1.

Examples of compounds of the formula (II) are diallylamines in which R⁴ is methyl, ethyl, isopropyl or n-propyl, isobutyl, n-butyl or tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl or
 30 decyl. Examples of long-chain radicals R⁴ are undecyl, dodecyl, tridecyl, pentadecyl, octadecyl and icosyl.

Examples of compounds of the formula (III) are
 N,N-dimethylaminomethyl (meth)acrylate,

- 35 N,N-diethylaminomethyl (meth)acrylate,
 N,N-dimethylaminoethyl (meth)acrylate,
 N,N-diethylaminoethyl (meth)acrylate,
 N,N-dimethylaminobutyl (meth)acrylate,
 N,N-diethylaminobutyl (meth)acrylate,
 40 N,N-dimethylaminohexyl (meth)acrylate,
 N,N-dimethylaminooctyl (meth)acrylate,
 N,N-dimethylaminododecyl (meth)acrylate,
 N-[3-(dimethylamino)propyl]methacrylamide,
 N-[3-(dimethylamino)propyl]acrylamide,
 45 N-[3-(dimethylamino)butyl]methacrylamide,
 N-[8-(dimethylamino)octyl]methacrylamide,
 N-[12-(dimethylamino)dodecyl]methacrylamide,

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N-[3-(diethylamino)propyl]methacrylamide,
N-[3-(diethylamino)propyl]acrylamide.

Preferred examples of monomers (a) are

- 5 3-methyl-1-vinylimidazolium chloride and methosulfate, dimethyldiallylammonium chloride and N,N-dimethylaminoethyl methacrylate and N-[3-(dimethylamino)propyl]methacrylamide which have been quaternized by methyl chloride, dimethyl sulfate or diethyl sulfate.

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Particularly preferred monomers (a) are 3-methyl-1-vinylimidazolium chloride and methosulfate and dimethyldiallylammonium chloride, very particular preference being given to 3-methyl-1-vinylimidazolium chloride and

- 15 methosulfate.

The monomers (a) can either be used in quaternized form as monomers or be polymerized in nonquaternized form, where, in the latter case, the resulting polymer is either quaternized or

- 20 protonated.

Suitable compounds for the quaternization of the compounds of the formula (I) to (III) are, for example, alkyl halides having 1 to 24 carbon atoms in the alkyl group, e.g. methyl chloride, methyl

- 25 bromide, methyl iodide, ethyl chloride, ethyl bromide, propyl chloride, hexyl chloride, dodecyl chloride, lauryl chloride and benzyl halides, in particular benzyl chloride and benzyl bromide. Further suitable quaternizing agents are dialkyl sulfates, in particular dimethyl sulfate or diethyl sulfate. The
- 30 quaternization of the basic monomers of the formula (I) to (III) can also be carried out with alkylene oxides, such as ethylene oxide or propylene oxide in the presence of acids.

The quaternization of the monomer or a polymer with one of said

- 35 quaternizing agents can be carried out by generally known methods.

Preferred quaternizing agents are: methyl chloride, dimethyl sulfate or diethyl sulfate.

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The quaternization of the polymer can be complete or else partial. The proportion of quaternized monomers (a) within the polymer can vary over a wide range and is, for example, about 20 to 100 mol%.

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- Suitable compounds for the protonation are, for example, mineral acids, such as HCl, H₂SO₄, H₃PO₄, and monocarboxylic acids, such as, for example, formic acid and acetic acid, dicarboxylic acids and polyfunctional carboxylic acids, such as, for example, oxalic acid and citric acid, and all other proton-releasing compounds and substances which are able to protonate the corresponding vinylimidazole or diallylamine. In particular, water-soluble acids are suitable for the protonation.
- 5
- 10 The protonation of the polymer can either take place after the polymerization or during the formulation of the cosmetic composition, during which a physiologically compatible pH is normally established.
- 15 Protonation is understood as meaning that at least some of the protonatable groups of the polymer, preferably 20 to 100 mol%, are protonated, such that an overall cationic charge of the polymer results.
- 20 Preferred monomers of group (b) are those compounds which dissolve to more than 5% by weight in water at a temperature of 25°C. If the polymers contain monomers of group (b), then they may be present in amounts up to 98.98% by weight. Particularly preferably, they are present in amounts of from 22 to 97.98% by
- 25 weight, in particular 45 to 85% by weight.

- Suitable water-soluble monomers (b) different from (a) are N-vinyl lactams, e.g. N-vinylpiperidone, N-vinylpyrrolidone and N-vinylcaprolactam, N-vinylacetamide, N-methyl-N-vinylacetamide,
- 30 N-vinylformamide, acrylamide, methacrylamide, N,N-dimethylacrylamide, N-methylolmethacrylamide, N-vinylloxazolidone, N-vinyltriazole, hydroxyalkyl (meth)acrylates, e.g. hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylates, or alkyl ethylene glycol
- 35 (meth)acrylates having 1 to 50 ethylene glycol units in the molecule.

- Particular preference is given to using N-vinyl lactams as monomers (b). Very particular preference is given to
- 40 N-vinylpyrrolidone.

- Also suitable are N-vinylimidazoles of the formula (I) in which R¹ to R³ are hydrogen, C₁-C₄-alkyl or phenyl and which are different from monomer (a), diallylamines of the formula (II), and
- 45 dialkylaminoalkyl (meth)acrylate and dialkylaminoalkyl(meth)acrylamides of the formula (III), e.g.

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dimethylaminoethyl methacrylate or
dimethylaminopropylmethacrylamide.

- Also suitable are unsaturated carboxylic acids and unsaturated
5 anhydrides, e.g. acrylic acid, methacrylic acid, crotonic acid,
itaconic acid, maleic acid, fumaric acid and their corresponding
anhydrides, and unsaturated sulfonic acids, such as, for example,
acrylamidomethylpropanesulfonic acid, and the salts of the
unsaturated acids, such as, for example, the alkali metal or
10 ammonium salts.

- Suitable monomers (c) different from monomers (a) and (b) are
C₁-C₄₀-alkyl esters of (meth)acrylic acid, where the esters are
derived from linear, branched-chain or carbocyclic alcohols, e.g.
15 methyl (meth)acrylate, ethyl (meth)acrylate, tert-butyl
(meth)acrylate, isobutyl (meth)acrylate, n-butyl (meth)acrylate,
stearyl (meth)acrylate, or esters of alkoxyated fatty alcohols,
e.g. C₁-C₄₀-fatty alcohols, reacted with ethylene oxide, propylene
oxide or butylene oxide, in particular C₁₀-C₁₈-fatty alcohols
20 reacted with 3 to 150 ethylene oxide units. Also suitable are
N-alkyl-substituted acrylamides with linear, branched-chain or
carbocyclic alkyl radicals, such as N-tert-butylacrylamide,
N-butylacrylamide, N-octylacrylamide, N-tert-octylacrylamide.
25 Also suitable are styrene, vinyl and allyl esters of
C₁-C₄₀-carboxylic acids, which may be linear, branched-chain or
carbocyclic, e.g. vinyl acetate, vinyl propionate, vinyl
neononanoate, vinyl neoundecanoic acid, vinyl t-butylbenzoate,
alkyl vinyl ethers, for example methyl vinyl ether, ethyl vinyl
30 ether, butyl vinyl ether, stearyl vinyl ether.

- Acrylamides, such as N-tert-butylacrylamide, N-butylacrylamide,
N-octylacrylamide, N-tert-octylacrylamide and N-alkyl-substituted
acrylamides with linear, branched-chain or carbocyclic alkyl
35 radicals, where the alkyl radical can have the meanings given
above for R⁴.

- Suitable monomers (c) are, in particular, C₁ to C₂₄-, very
particularly C₁ to C₁₀-, alkyl esters of (meth)acrylic acid, e.g.
40 methyl (meth)acrylate, ethyl (meth)acrylate, tert-butyl
(meth)acrylate, isobutyl (meth)acrylate, n-butyl (meth)acrylate
and acrylamides, such as N-tert-butylacrylamide or
N-tert-octylacrylamide.

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If the polymers contain monomers of group (c), then they may be present therein in amounts up to 50% by weight, in particular up to 40% by weight, preferably up to 30% by weight.

- 5 Monomers (d), which have a crosslinking function, are compounds with at least 2 ethylenically unsaturated, nonconjugated double bonds in the molecule.

Suitable crosslinkers (d) are, for example, acrylic esters, 10 methacrylic esters, allyl ethers or vinyl ethers of at least dihydric alcohols. The OH groups of the parent alcohols may be in completely or partially etherified or esterified form; however, the crosslinkers contain at least two ethylenically unsaturated groups.

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- Examples of the parent alcohols are dihydric alcohols, such as 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, but-2-ene-1,4-diol, 1,2-pentanediol, 1,5-pentanediol, 20 1,2-hexanediol, 1,6-hexanediol, 1,10-decanediol, 1,2-dodecanediol, 1,12-dodecanediol, neopentylglycol, 3-methylpentane-1,5-diol, 2,5-dimethyl-1,3-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-bis(hydroxymethyl)cyclohexane, 25 neopentylglycol mono(hydroxypivalate), 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis[4-(2-hydroxypropyl)phenyl]propane, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 30 3-thiopentane-1,5-diol, and polyethylene glycols, polypropylene glycols and polytetrahydrofurans with molecular weights of in each case 200 to 10 000. Apart from the homopolymers of ethylene oxide and/or propylene oxide, it is also possible to use block copolymers of ethylene oxide or propylene oxide, or copolymers 35 which contain ethylene oxide and propylene oxide groups in incorporated form. Examples of parent alcohols with more than two OH groups are trimethylolpropane, glycerol, pentaerythritol, 1,2,5-pentanetriol, 1,2,6-hexanetriol, triethoxycyanuric acid, sorbitan, sugars, such as sucrose, glucose, mannose. The 40 polyhydric alcohols can of course also be used following reaction with ethylene oxide or propylene oxide, as the corresponding ethoxylates or propoxylates respectively. The polyhydric alcohols can also firstly be converted into the corresponding glycidyl ethers by reaction with epichlorohydrin.

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Further suitable crosslinkers are the vinyl esters or the esters of monohydric, unsaturated alcohols with ethylenically unsaturated C₃- to C₆-carboxylic acids, for example acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid.

- 5 Examples of such alcohols are allyl alcohol, 1-buten-3-ol, 5-hexen-1-ol, 1-octen-3-ol, 9-decen-1-ol, dicyclopentenyl alcohol, 10-undecen-1-ol, cinnamyl alcohol, citronellol, crotyl alcohol or cis-9-octadecen-1-ol. It is, however, also possible to esterify the monohydric, unsaturated alcohols with polybasic
- 10 carboxylic acids, for example malonic acid, tartaric acid, trimellitic acid, phthalic acid, terephthalic acid, citric acid or succinic acid.

- Further suitable crosslinkers are esters of unsaturated
- 15 carboxylic acids with the above-described polyhydric alcohols, for example oleic acid, crotonic acid, cinnamic acid or 10-undecenoic acid.

- Also suitable as monomers (d) are straight-chain or branched,
- 20 linear or cyclic, aliphatic or aromatic hydrocarbons which have at least two double bonds which, in the case of aliphatic hydrocarbons, must not be conjugated, e.g. divinylbenzene, divinyltoluene, 1,7-octadiene, 1,9-decadiene, 4-vinyl-1-cyclohexene, trivinylcyclohexane or polybutadienes with
- 25 molecular weights of from 200 to 20 000.

- Also suitable as crosslinkers are acrylamides, methacrylamides and N-allylamines of at least difunctional amines. Such amines, are, for example, 1,2-diaminomethane, 1,2-diaminoethane,
- 30 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,12-dodecanediamine, piperazine, diethylenetriamine or isophoronediamine. Also suitable are the amides of allylamine and unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, or at least dibasic carboxylic
- 35 acids, as described above.

- Also suitable as crosslinkers are triallylamine and triallylmonoalkylammonium salts, e.g. triallylmethylammonium chloride or methyl sulfate.

- 40 Also suitable are N-vinyl compounds of urea derivatives, at least difunctional amides, cyanurates or urethanes, for example of urea, ethyleneurea, propyleneurea or tartramide, e.g. N,N'-divinylethyleneurea or N,N'-divinylpropyleneurea.

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Further suitable crosslinkers are divinylidioxane, tetraallylsilane or tetravinylsilane.

It is of course also possible to use mixtures of the
5 abovementioned compounds. Preference is given to using those crosslinkers which are soluble in the monomer mixture.

Particularly preferred crosslinkers are, for example, methylenebisacrylamide, triallylamine and triallylalkylammonium
10 salts, divinylimidazole, pentaerythritol triallyl ether, N,N'-divinylethyleneurea, reaction products of polyhydric alcohols with acrylic acid or methacrylic acid, methacrylic esters and acrylic esters of polyalkylene oxides or polyhydric alcohols which have been reacted with ethylene oxide and/or
15 propylene oxide and/or epichlorohydrin.

Very particularly preferred crosslinkers are pentaerythritol triallyl ether, methylenebisacrylamide, N,N'-divinylethyleneurea, triallylamine and triallylmonoalkylammonium salts, and acrylic
20 esters of glycol, butanediol, trimethylolpropane or glycerol, or acrylic esters of glycol, butanediol, trimethylolpropane or glycerol reacted with ethylene oxide and/or epichlorohydrin.

The monomers (a) to (e) can in each case be used individually or
25 in a mixture with other monomers from the same group.

The copolymerization takes place in the presence of at least one regulator (e). The term regulator (polymerization regulator) is used to describe compounds with high transfer constants.
30 Regulators accelerate chain transfer reactions and thus effect a lowering of the degree of polymerization of the resulting polymers without influencing the net reaction rate.

With the regulators, it is possible to differentiate between
35 mono-, bi- or polyfunctional regulators, depending on the number of functional groups in the molecule which can lead to one or more chain transfer reactions. Suitable regulators are described in detail, for example, by K.C. Berger and G. Brandrup in J. Brandrup, E.H. Immergut, Polymer Handbook, 3rd edition, John
40 Wiley & Sons, New York, 1989, p. II/81 - II/141.

Suitable regulators are, for example, aldehydes, such as formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde.

Other regulators which can be used are: formic acid, its salts or
45 esters, 2,5-diphenyl-1-hexene, ammonium formate, hydroxylammonium sulfate and hydroxylammonium phosphate.

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Further suitable regulators are halogen compounds, such as alkyl halides, such as tetrachloromethane, chloroform, bromotrichloromethane, bromoform, allyl bromide, and benzyl compounds, such as benzyl chloride or benzyl bromide.

- 5 Further suitable regulators are allyl compounds, such as, for example, allyl alcohol, functional allyl ethers, such as allyl ethoxylates, alkyl allyl ethers, or glycerol monoallyl ether.

The regulators used are preferably compounds which contain sulfur
10 in bonded form.

- Compounds of this type are, for example, inorganic hydrogensulfites, disulfites and dithionites or organic sulfides, disulfides, polysulfides, sulfoxides, sulfones. The following
15 regulators are mentioned by way of example: di-n-butyl sulfide, di-n-octyl sulfide, diphenyl sulfide, thiodiglycol, ethylthioethanol, diisopropyl disulfide, di-n-butyl disulfide, di-n-hexyl disulfide, diacetyl disulfide, diethanol sulfide, di-t-butyl trisulfide, dimethyl sulfoxide, dialkyl sulfide,
20 dialkyl disulfide and/or diaryl sulfide.

Particular preference is given to organic compounds which contain sulfur in bonded form.

- 25 Preferably, compounds used as polymerization regulators are thiols (compounds which contain sulfur in the form of SH groups, also referred to as mercaptans). Preferred regulators are mono-, bi- and polyfunctional mercaptans, mercaptoalcohols and/or mercaptocarboxylic acids.

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- Examples of these compounds are allyl thioglycolates, ethyl thioglycolate, cysteine, 2-mercaptoethanol, 1,3-mercaptopropanol, 3-mercaptopropane-1,2-diol, 1,4-mercaptobutanol, mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid,
35 thioglycerol, thioacetic acid, thiourea and alkyl mercaptans, such as n-butyl mercaptan, n-hexyl mercaptan or n-dodecyl mercaptan.

- Particularly preferred thiols are cysteine, 2-mercaptoethanol,
40 1,3-mercaptopropanol, 3-mercaptopropane-1,2-diol, thioglycerol, thiourea.

- Examples of bifunctional regulators which contain two sulfurs in bonded form are bifunctional thiols, such as, for example,
45 dimercaptopropanesulfonic acid (sodium salt), dimercaptosuccinic acid, dimercapto-1-propanol, dimercaptoethane, dimercaptopropane,

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dimercaptobutane, dimercaptopentane, dimercaptohexane, ethylene glycol bis-thioglycolates and butanediol bis-thioglycolate.

- 5 Examples of polyfunctional regulators are compounds which contain more than two sulfurs in bonded form. Examples thereof are trifunctional and/or tetrafunctional mercaptans.

Preferred trifunctional regulators are trifunctional mercaptans, such as, for example,

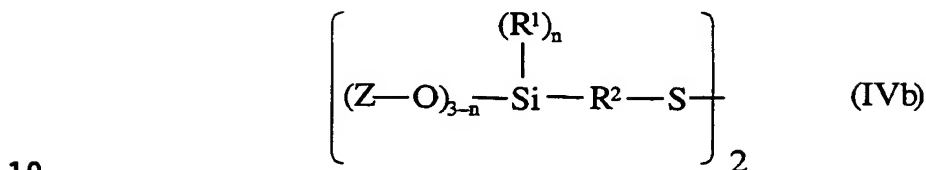
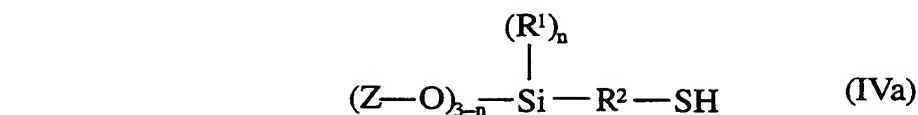
- 10 trimethylolpropane tris(2-mercaptoethanoate), trimethylolpropane tris(3-mercaptopropionate), trimethylolpropane tris(4-mercaptobutanoate), trimethylolpropane tris(5-mercaptopentanoate), trimethylolpropane tris(6-mercaptohexanoate), trimethylolpropane
15 tris(2-mercaptoacetate).

- Glyceryl thioglycolate, glyceryl thiopropionate, glyceryl thioethoxide, glyceryl thiobutanoate,
1,1,1-propanetriyl tris(mercaptoacetate), 1,1,1-propanetriyl
20 tris(mercaptoethanoate), 1,1,1-propanetriyl tris(mercaptopropionate), 1,1,1-propanetriyl tris(mercaptobutanoate),
2-hydroxymethyl-2-methyl-1,3-propanediol tris(mercaptoacetate),
2-hydroxymethyl-2-methyl-1,3-propanediol tris(mercaptoethanoate),
25 2-hydroxymethyl-2-methyl-1,3-propanediol tris(mercaptopropionate),
2-hydroxymethyl-2-methyl-1,3-propanediol tris(mercaptobutanoate).

- Particularly preferred trifunctional regulators are
30 glyceryl thioglycolate, trimethylolpropane tris(2-mercaptoacetate, 2-hydroxymethyl-2-methyl-1,3-propanediol tris(mercaptoacetate).

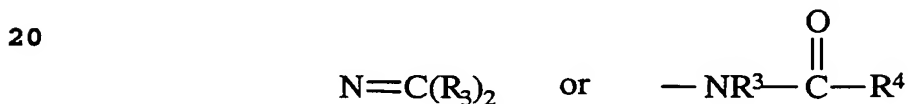
- Preferred tetrafunctional mercaptans are
35 pentaerythritol tetraquis(2-mercaptoacetate), pentaerythritol tetraquis(2-mercaptoethanoate), pentaerythritol tetraquis(3-mercaptopropionate), pentaerythritol tetraquis(4-mercaptobutanoate), pentaerythritol tetraquis(5-mercaptopentanoate), pentaerythritol
40 tetraquis(6-mercaptohexanoate).

- Further suitable polyfunctional regulators are Si compounds which are formed by reacting compounds of the formula (IVa). Also suitable as polyfunctional regulators are Si compounds of the
45 formula (IVb).



in which

- n is a value from 0 to 2,
 R¹ is a C₁-C₁₆-alkyl group or phenyl group
 15 R² is a C₁-C₁₈-alkyl group, the cyclohexyl group or phenyl group,
 Z is a C₁-C₁₈ alkyl group, C₂-C₁₈-alkylene group or
 C₂-C₁₈-alkynyl group whose carbon atoms may be replaced by
 nonadjacent oxygen or halogen atoms, or is one of the groups



in which

- 25 R₃ is a C₁-C₁₂-alkyl group and
 R₄ is a C₁-C₁₈-alkyl group.

Particular preference is given to the compounds IVa, including,
 primarily, mercaptopropyltrimethoxysilane and
 30 mercaptopropyltriethoxysilane.

All of the regulators mentioned can be used individually or in
 combination with one another.

- 35 In a preferred embodiment, 0.1 to 5 parts by weight, preferably
 0.2 to 2 parts by weight, and in particular 0.25 to 1 part by
 weight, of a polymerization regulator (e) is used per 1 part by
 weight of a crosslinker (monomer (d)).

40 The present invention further provides polymers obtainable by

(i) free-radically initiated copolymerization of monomer mixtures
 of

- 45 (a) at least one cationic monomer or quaternizable monomer
 (b) optionally at least one water-soluble monomer,

17

- (c) optionally at least one further free-radically copolymerizable monomer
- (d) at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds, and
- (e) at least one polyfunctional regulator

5

- (ii) subsequent quaternization or protonation of the polymer if the monomer (a) used is a nonquaternized monomer or an only partially quaternized monomer.

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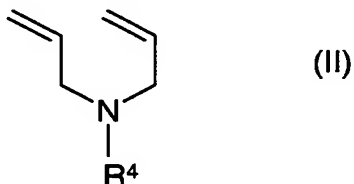
The present invention further provides polymers obtainable by

- (i) free-radically initiated copolymerization of monomer mixtures of

15

- (a) at least one cationic monomer or quaternizable monomer chosen from the group consisting of diallylamines of the formula (II) in which R^4 is C_1-C_{24} -alkyl

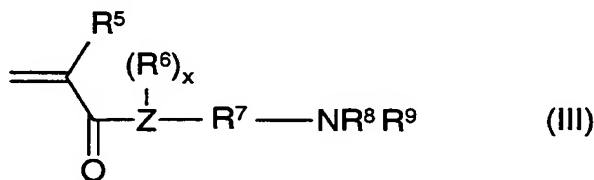
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25

and N,N-dialkylaminoalkyl acrylates and methacrylates and N,N-dialkylaminoalkylacrylamides and -methacrylamides of the formula (III),

30



35

where R^5 , R^6 , independently, are a hydrogen atom or a methyl radical, R^7 is an alkylene radical having 1 to 24 carbon atoms, optionally substituted by alkyl radicals, and R^8 , R^9 are C_1-C_{24} -alkyl radicals. Z is a nitrogen atom together with $x = 1$ or is an oxygen atom together with $x = 0$,

40

- (b) optionally at least one water-soluble monomer,
- (c) optionally at least one further free-radically copolymerizable monomer,
- (d) at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds, and

45

(e) at least one regulator

- (ii) subsequent quaternization or protonation of the polymer if the monomer (a) used is a nonquaternized monomer or an only partially quaternized monomer.

WO 93/25592 describes crosslinked polymers of quaternized aminoalkylacrylates or aminoalkylacrylamides with vinyl lactams. These polymers are prepared without regulators.

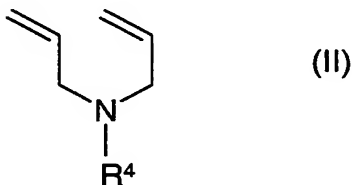
- The invention further provides a process for the preparation of polymers by free-radically initiated copolymerization of a monomer mixture of

- (a) at least one cationic monomer or quaternizable monomer
(b) optionally at least one water-soluble monomer,
(c) optionally at least one further free-radically copolymerizable monomer
(d) at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds, in the presence of a polyfunctional regulator (e)

- and subsequent quaternization or protonation of the polymer if the monomer (a) used is a nonquaternized monomer or an only partially quaternized monomer.

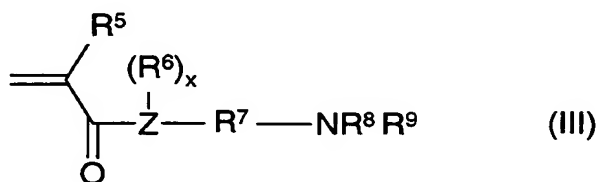
The invention further provides a process for the preparation of polymers by free-radically initiated copolymerization of a monomer mixture of

- (a) at least one cationic monomer or quaternizable monomer chosen from the group consisting of diallylamines of the formula (II) in which R^4 is C_1 - C_{24} -alkyl



19

and N,N-dialkylaminoalkyl acrylates and methacrylates and N,N-dialkylaminoalkylacrylamides and -methacrylamides of the formula (III),



where R⁵, R⁶, independently, are a hydrogen atom or a methyl radical, R⁷ is an alkylene radical having 1 to 24 carbon atoms, optionally substituted by alkyl radicals, and R⁸, R⁹ are C₁-C₂₄-alkyl radicals. Z is a nitrogen atom together with x = 1 or is an oxygen atom together with x = 0,

- (b) optionally at least one water-soluble monomer,
- (c) optionally at least one further free-radically copolymerizable monomer,
- (d) at least one crosslinking monomer having at least two ethylenically unsaturated, nonconjugated double bonds,

in the presence of a regulator (e)

- and subsequent quaternization or protonation of the polymer, if the monomer (a) is a nonquaternized monomer or an only partially quaternized monomer.

The polymers can be prepared by processes of free-radically initiated polymerization known per se, e.g. by solution polymerization, emulsion polymerization, suspension polymerization, precipitation polymerization, inverse suspension polymerization or inverse emulsion polymerization, without the methods which can be used being limited thereto.

The monomers (a), (d), (e) and optionally (b) and (c) are copolymerized according to a type of solution polymerization in water and/or polar organic solvents. Suitable polar organic solvents are, for example, water-miscible compounds, such as tetrahydrofuran, N-methylpyrrolidone, dioxane, dimethyl sulfoxide, acetone, glycols, such as ethylene glycol, propylene glycol, 1,4-butanediol, diethylene glycol, triethylene glycol, tetraethylene glycol and block copolymers of ethylene oxide and propylene oxide, and etherified polyalkylene glycols which are obtainable, for example, by alkylation of alkylene glycols and polyalkylene glycols. Suitable compounds are, for example, the glycols or polyethylene glycols containing C₁- to C₄-alkyl end

groups. The etherification can be carried out on one side or on both sides. Other suitable solvents are alcohols having 1 to 4 carbon atoms or acetone. It is possible to use either a single solvent, or to carry out the copolymerization also in the
5 presence of solvent mixtures. Particularly preferred solvents are water, C₁- to C₃-alcohols, such as methanol, ethanol, isopropanol and n-propanol, and mixtures of said solvents. The solvents are usually used in an amount such that copolymer solutions with a copolymer content of from 5 to 80% by weight, preferably 10 to
10 60% by weight, are obtained.

In a preferred embodiment, the regulator (e), optionally in the form of a solution in water and/or a C₁-C₄-alcohol, is metered into the reaction mixture.

15 In a preferred embodiment, the processes according to the invention are carried out as batch procedures. In this connection, it is preferred to introduce the regulator (e) into the initial charge.

20 In a preferred embodiment, the processes according to the invention are carried out as feed procedures. In this connection, individual or all of the reactants are added in totality or partially, batchwise or continuously, together or in separate
25 feeds, to a reaction mixture. Thus, for example, a solution of the polymerization regulator and an initiator solution can be added continuously or batchwise to a mixture of the monomers and a solvent at the polymerization temperature within the stated time. It is, however, also possible to meter in a mixture of
30 regulator and initiator into the initial charge heated to the polymerization temperature. Another variant consists in adding the initiator to the initial charge below or at the polymerization temperature and only introducing the regulator or a solution of the regulator into the reaction mixture within a
35 pregiven period after the polymerization temperature has been reached. In a further variant, the initiator and the crosslinker (d) are added to a mixture of regulator (e), monomer (a) and optionally monomers (b) and (c) and a solvent after the polymerization temperature has been reached. It is also possible
40 to heat the initial charge to the polymerization temperature and then to add regulator (e), initiator and monomers (d) in separate feeds or together. It is of course also possible to add regulator (e), initiator, monomers (d) and monomers (a) and optionally monomers (b) and (c) to an initial charge heated to the
45 polymerization temperature. Preference is given to using water or a mixture of water and at least some of the monomers (a) and optionally (b) and (c), and optionally further components as the

initial charge. Particular preference here is given to a procedure in which the polymerization regulators (e) are metered in continuously or in portions during the polymerization of the monomers.

5

The polymerization is usually carried out at temperatures of from 20°C to 130°C and at atmospheric pressure or under autogenous pressure.

- 10 Initiators which can be used for the free-radical polymerization are the water-soluble and water-insoluble peroxo and/or azo compounds customary for this purpose, for example alkali metal or ammonium peroxydisulfates, dibenzoyl peroxide, tert-butyl perpivalate, tert-butyl-per-2-ethylhexanoate, di-tert-butyl peroxide, tert-butyl hydroperoxide, azobisisobutyronitrile, azobis(2-amidinopropane) dihydrochloride or 2,2'-azobis(2-methylbutyronitrile). Also suitable are initiator mixtures or redox initiator systems, such as, for example, ascorbic acid/iron(II) sulfate /sodium peroxodisulfate,
- 15 tert-butyl hydroperoxide/sodium disulfite, tert-butyl hydroperoxide/sodium hydroxymethanesulfinate. The initiators can be used in the customary amounts, for example 0.05 to 5% by weight, based on the amount of the monomers to be polymerized.

- 25 The molecular weight and the K value of the polymers can be varied within a wide range in a manner known per se through the choice of polymerization conditions, for example polymerization time, polymerization temperature or initiator concentration, and by the content of crosslinker, and regulators.

30

In a preferred embodiment, the person skilled in the art chooses the reaction conditions such that polymers are formed which have a viscosity below 15 000 mPas (measured in accordance with Brookfield, spindle 4, 12 rpm, 25°C).

35

The concentration of the monomers in the reaction medium is usually 5 to 60% by weight and is preferably in the range from 10 to 45% by weight. The polymerization is carried out such that visible gelling of the reaction mixture does not occur. Should

- 40 gel particles form, these have a diameter of less than 1 mm, preferably less than 500 nm, determined by scattered light measurement in the chosen reaction medium. The resulting copolymers are homogeneously soluble in the reaction medium.

- 45 The K values of the polymers are in a range between 10 and 350, preferably 20 and 200 and particularly preferably 35 to 110. The K values are measured in accordance with Fikentscher,

Cellulosechemie, vol. 13, pp. 58-64 (1932) at 25°C at 0.1% strength in 5% by weight sodium chloride solution.

The mixtures formed during the polymerization can, following the
5 polymerization process, be subjected to a physical or chemical
after-treatment. Such processes are, for example, the known
processes for reducing residual monomers, such as, for example,
after-treatment by adding polymerization initiators or mixtures
10 of two or more polymerization initiators at suitable temperatures
or heating the polymerization solution to temperatures above the
polymerization temperature, an after-treatment of the polymer
solution using steam or stripping with nitrogen or treatment of
the reaction mixture with oxidizing or reducing reagents,
adsorption processes, such as the adsorption of impurities onto
15 selected media, such as, for example, activated carbon, or
ultrafiltration. It is also possible to follow with known work-up
steps, for example suitable drying processes, such as spray,
freeze or roller drying or agglomeration processes following the
drying. The mixtures with a low content of residual monomer
20 obtained by the process according to the invention can also be
sold directly.

The polymers according to the invention can advantageously be
used in cosmetic preparations, in particular hair cosmetic
25 preparations.

The term "cosmetic preparations" is understood broadly and means
all those preparations which are suitable for application to skin
and/or hair and/or nails and pursue a purpose other than a purely
30 medicinal-therapeutic purpose.

The polymers according to the invention can be used in skin
cosmetic preparations.

35 For example, the polymers according to the invention are used in
cosmetic compositions for cleansing the skin. Such cosmetic
cleansers are chosen from bar soaps, such as toilet soaps, curd
soaps, transparent soaps, luxury soaps, deodorant soaps, cream
soaps, baby soaps, skin protection soaps, abrasive soaps and
40 syndets, liquid soaps, such as pasty soaps, soft soaps and
washing pastes, and liquid washing, shower and bath preparations,
such as washing lotions, shower preparations and gels, foam
baths, oil baths and scrub preparations.

23

The polymers according to the invention are preferably used in cosmetic compositions for care and protection of the skin, in nail care compositions and in preparations for decorative cosmetics.

5

Particular preference is given to the use in skin care compositions, intimate care compositions, foot care compositions, deodorants, sunscreen compositions, repellents, shaving compositions, hair-removal compositions, antiacne compositions, 10 make-up, mascara, lipsticks, eyeshadows, kohl pencils, eyeliners, blushers, powders and eyebrow pencils.

The skin care compositions are, in particular, in the form of W/O or O/W skin creams, day and night creams, eye creams, face 15 creams, antiwrinkle creams, moisturizing creams, bleaching creams, vitamin creams, skin lotions, care lotions and moisturizing lotions.

In the cosmetic preparations, the polymers according to the 20 invention can develop particular effects. The polymers can, inter alia, contribute to the moistening and conditioning of the skin and to improving the feel of the skin. The polymers can also act as thickeners in the formulations. By adding the polymers according to the invention, it is possible to achieve a 25 considerable improvement in the skin compatibility in certain formulations.

The copolymers according to the invention are present in the skin cosmetic preparations in a proportion of about 0.001 to 20% by 30 weight, preferably 0.01 to 10% by weight, very particularly preferably 0.1 to 5% by weight, based on the total weight of the composition.

Depending on the field of use, the compositions according to the 35 invention can be applied in a form suitable for skin care, such as, for example, in the form of a cream, foam, gel, stick, powder, mousse, milk or lotion.

In addition to the polymers according to the invention and 40 suitable solvents, the skin cosmetic preparations may also comprise additives customary in cosmetics, such as emulsifiers, preservatives, perfume oils, cosmetic active ingredients, such as phytantriol, vitamins A, E and C, retinol, bisabolol, panthenol, sunscreens, bleaches, colorants, tints, tanning agents (e.g. 45 dihydroxyacetone), collagen, protein hydrolyzates, stabilizers, pH regulators, dyes, salts, thickeners, gel formers, bodying

agents, silicones, humectants, refatting agents and further customary additives.

- Suitable solvents are, in particular, water and lower
- 5 monoalcohols or polyols having 1 to 6 carbon atoms or mixtures thereof; preferred monoalcohols or polyols are ethanol, isopropanol, propylene glycol, glycerol and sorbitol.

- Further customary additives which may be present are fatty
- 10 bodies, such as mineral and synthetic oils, such as, for example, paraffins, silicone oils and aliphatic hydrocarbons with more than 8 carbon atoms, animal and vegetable oils, such as, for example, sunflower oil, coconut oil, avocado oil, olive oil, lanolin, or waxes, fatty acids, fatty acid esters, such as, for
- 15 example, triglycerides of C₆-C₃₀-fatty acids, wax esters, such as, for example, jojoba oil, fatty alcohols, vaseline, hydrogenated lanolin and acetylated lanolin. It is of course also possible to use mixtures thereof.

- 20 Customary thickeners in such formulations are crosslinked polyacrylic acids and derivatives thereof, polysaccharides, such as xanthan gum, agar agar, alginates or Tyloses, carboxymethylcellulose or hydroxycarboxymethylcellulose, fatty alcohols, monoglycerides and fatty acids, polyvinyl alcohol and
- 25 polyvinylpyrrolidone.

The polymers according to the invention can also be mixed with conventional polymers if specific properties are to be set.

- 30 Suitable conventional polymers are, for example, anionic, cationic, amphoteric and neutral polymers.

- Examples of anionic polymers are homo- and copolymers of acrylic acid and methacrylic acid or salts thereof, copolymers of acrylic
- 35 acid and acrylamide and salts thereof; sodium salts of polyhydroxycarboxylic acids, water-soluble or water-dispersible polyesters, polyurethanes and polyureas. Particularly suitable polymers are copolymers of t-butyl acrylate, ethyl acrylate, methacrylic acid (e.g. Luvimer[®] 100P), copolymers of ethyl
- 40 acrylate and methacrylic acid (e.g. Luvimer[®] MAE), copolymers of N-tert-butylacrylamide, ethyl acrylate, acrylic acid (Ultrahold[®] 8, strong), copolymers of vinyl acetate, crotonic acid and optionally further vinyl esters (e.g. Luviset[®] products), maleic anhydride copolymers, optionally reacted with alcohols, anionic
- 45 polysiloxanes, e.g. carboxyfunctional, copolymers of vinylpyrrolidone, t-butyl acrylate, methacrylic acid (e.g. Luviskol[®] VBM), copolymers of acrylic acid and methacrylic acid

25

with hydrophobic monomers, such as, for example C₄-C₃₀-alkyl esters of meth(acrylic acid), C₄-C₃₀-alkyl vinyl esters, C₄-C₃₀-alkyl vinyl ethers and hyaluronic acid.

- 5 Further suitable polymers are cationic polymers with the INCI name Polyquaternium, e.g. copolymers of vinylpyrrolidone/N-vinylimidazolium salts (Luviquat[®] FC, Luviquat[®] HM, Luviquat[®] MS, Luviquat[®] Care), copolymers of N-vinylpyrrolidone/dimethylaminoethyl methacrylate, quaternized
10 with diethyl sulfate (Luviquat[®] PQ 11), copolymers of N-vinylcaprolactam/N-vinylpyrrolidone/N-vinylimidazolium salts (Luviquat[®] Hold); cationic cellulose derivatives (Polyquaternium-4 and -10), acrylamide copolymers (Polyquaternium-7) and chitosan.

- 15 Also suitable as further polymers are neutral polymers, such as polyvinylpyrrolidones, copolymers of N-vinylpyrrolidone and vinyl acetate and/or vinyl propionate, polysiloxanes, polyvinylcaprolactam and copolymers with N-vinylpyrrolidone,
20 polyethyleneimines and salts thereof, polyvinylamines and salts thereof, cellulose derivatives, polyaspartic acid salts and derivatives.

- To establish certain properties, the preparations can
25 additionally also comprise conditioning substances based on silicone compounds. Suitable silicone compounds are, for example, polyalkylsiloxanes, polyarylsiloxanes, polyaryalkylsiloxanes, polyether siloxanes or silicone resins.
- 30 The copolymers according to the invention are used in cosmetic preparations, the preparation of which is carried out in accordance with rules familiar to the person skilled in the art.

- Such formulations are advantageously in the form of emulsions,
35 preferably in the form of water-in-oil (W/O) or oil-in-water (O/W) emulsions. However, according to the invention, it is also possible and in some instances advantageous to choose other types of formulation, for example hydrodispersions, gels, oils, oleogels, multiple emulsions, for example in the form of W/O/W or
40 O/W/O emulsions, anhydrous ointments or ointment bases etc.

The emulsions which can be used according to the invention are prepared by known methods.

- 45 In addition to the copolymer according to the invention, the emulsions comprise customary constituents, such as fatty alcohols, fatty acid esters and, in particular, fatty acid

triglycerides, fatty acids, lanolin and derivatives thereof, natural or synthetic oils or waxes and emulsifiers in the presence of water.

- 5 The choice of emulsion type-specific additives and the preparation of suitable emulsions is described, for example, in Schrader, Grundlagen und Rezepturen der Kosmetika [Fundamentals and Formulations of Cosmetics], Hüthig Buch Verlag, Heidelberg, 2nd edition, 1989, third part, to which reference is expressly
10 made here.

Thus, a skin cream which can be used according to the invention can, for example, be in the form of a W/O emulsion. Such an emulsion comprises an aqueous phase which is emulsified in an oil
15 or fatty phase by means of a suitable emulsifier system.

The concentration of the emulsifier system in this type of emulsion is about 4 to 35% by weight, based on the total weight of the emulsion; the fatty phase constitutes about 20 to 60% by
20 weight and the aqueous phase about 20 to 70% by weight, in each case based on the total weight of the emulsion. The emulsifiers are those which are usually used in this type of emulsion. They are, for example, chosen from: C₁₂-C₁₈-sorbitan fatty acid esters; esters of hydroxystearic acid and C₁₂-C₃₀-fatty alcohols; mono-
25 and diesters of C₁₂-C₁₈-fatty acids and glycerol or polyglycerol; condensates of ethylene oxide and propylene glycols; oxypropylenated/oxyethylenated C₁₂-C₂₀-fatty alcohols; polycyclic alcohols, such as sterols; aliphatic alcohols with a high molecular weight, such as lanolin; mixtures of
30 oxypropylenated/polyglycerolated alcohols and magnesium isostearate; succinic esters of polyoxyethylenated or polyoxypropylenated fatty alcohols; and mixtures of magnesium lanolate, calcium lanolate, lithium lanolate, zinc lanolate or aluminum lanolate and hydrogenated lanolin or lanolin alcohol.

35 Suitable fatty components which may be present in the fatty phase of the emulsions include hydrocarbon oils, such as paraffin oil, purcellin oil, perhydrosqualene and solutions of microcrystalline waxes in these oils; animal or vegetable oils, such as sweet
40 almond oil, avocado oil, calophyllum oil, lanolin and derivatives thereof, castor oil, sesame oil, olive oil, jojoba oil, karité oil, hoplostethus oil; mineral oils whose distillation start under atmospheric pressure is at about 250°C and whose distillation end point is at 410°C, such as, for example, vaseline
45 oil; esters of saturated or unsaturated fatty acids, such as alkyl myristates, e.g. isopropyl myristate, butyl myristate or cetyl myristate, hexadecyl stearate, ethyl palmitate or isopropyl

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palmitate, octanoic or decanoic acid triglycerides and cetyl ricinoleate.

5 The fatty phase can also comprise silicone oils soluble in other oils, such as dimethylpolysiloxane, methylphenylpolysiloxane and the silicone-glycol copolymer, fatty acids and fatty alcohols.

10 In order to favor the retention of oils, it is also possible to use waxes, such as, for example, carnauba wax, candellila wax, beeswax, microcrystalline wax, ozokerite wax and Ca, Mg and Al oleates, myristates, linoleates and stearates.

15 In general, these water-in-oil emulsions are prepared by adding the fatty phase and the emulsifier to the batch container. The container is heated at a temperature of from 70 to 75°C, then the oil-soluble ingredients are added and, with stirring, water is added which has been heated beforehand to the same temperature and in which the water-soluble ingredients have been dissolved beforehand; the mixture is stirred until an emulsion of the
20 desired fineness is obtained, which is then left to cool to room temperature, if necessary with a lesser amount of stirring.

In addition, a care emulsion according to the invention can be in the form of an O/W emulsion. Such an emulsion usually comprises
25 an oil phase, emulsifiers which stabilize the oil phase in the water phase, and an aqueous phase which is usually present in thickened form.

The aqueous phase of the O/W emulsion of the preparations
30 according to the invention optionally comprises

- alcohols, diols or polyols and ethers thereof, preferably ethanol, isopropanol, propylene glycol, glycerol, ethylene glycol monoethyl ether;
35
- customary thickeners or gel formers, such as, for example, crosslinked polyacrylic acids and derivatives thereof, polysaccharides, such as xanthan gum, or alginates, carboxymethylcellulose or hydroxycarboxymethylcellulose,
40 fatty alcohols, polyvinyl alcohol and polyvinylpyrrolidone.

The oil phase comprises oil components customary in cosmetics, such as, for example:

- 45 - esters of saturated and/or unsaturated, branched and/or unbranched C₃-C₃₀-alkanecarboxylic acids and saturated and/or unsaturated, branched and/or unbranched C₃-C₃₀-alcohols, of

28

- aromatic carboxylic acids and saturated and/or unsaturated, branched and/or unbranched C₃-C₃₀-alcohols, for example isopropyl myristate, isopropyl stearate, hexyldecyl stearate, oleyl oleate; and also synthetic, semisynthetic and natural mixtures of such esters, such as jojoba oil;
- 5
- branched and/or unbranched hydrocarbons and hydrocarbon waxes;
- 10
- silicone oils, such as cyclomethicone, dimethylpolysiloxane, diethylpolysiloxane, octamethylcyclotetrasiloxane, and mixtures thereof;
 - dialkyl ethers;
- 15
- mineral oils and mineral waxes;
 - triglycerides of saturated and/or unsaturated, branched and/or unbranched C₈-C₂₄-alkanecarboxylic acids; they can be
- 20
- chosen from synthetic, semisynthetic or natural oils, such as olive oil, palm oil, almond oil or mixtures.

Suitable emulsifiers are preferably O/W emulsifiers, such as polyglycerol esters, sorbitan esters or partially esterified

25 glycerides.

The preparation can take place by melting the oil phase at about 80°C; the water-soluble constituents are dissolved in hot water, and added to the oil phase slowly and with stirring; the mixture

30 is then homogenized and stirred until cold.

The polymers according to the invention are also suitable for use in washing and shower gel formulations and bath preparations.

35 In addition to the polymers according to the invention, such formulations usually comprise anionic surfactants as base surfactants and amphoteric and nonionic surfactants as cosurfactants, and also lipids, perfume oils, dyes, organic acids, preservatives and antioxidants, and also

40 thickeners/gelling agents, skin conditioning agents and humectants.

All anionic, neutral, amphoteric or cationic surfactants used customarily in body-cleansing compositions can be used in the

45 washing, shower and bath preparations.

The formulations comprise 2 to 50% by weight of surfactants, preferably 5 to 40% by weight, particularly preferably 8 to 30% by weight.

- 5 Suitable anionic surfactants are, for example, alkyl sulfates, alkyl ether sulfates, alkylsulfonates, alkylarylsulfonates, alkyl succinates, alkyl sulfosuccinates, N-alkoyl sarcosinates, acyl taurates, acyl isethionates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, alpha-olefinsulfonates, in particular the alkali metal and alkaline earth metal salts, e.g. sodium, potassium, magnesium, calcium, and ammonium and triethanolamine salts. The alkyl ether sulfates, alkyl ether phosphates and alkyl ether carboxylates can have between 1 to 10 ethylene oxide or propylene oxide units, preferably 1 to 3
- 10 ethylene oxide units, in the molecule.
- 15

- Suitable are, for example, sodium lauryl sulfate, ammonium lauryl sulfate, sodium lauryl ether sulfate, ammonium lauryl ether sulfate, sodium lauryl sarcosinate, sodium oleyl succinate,
- 20 ammonium lauryl sulfosuccinate, sodium dodecylbenzenesulfonate, triethanolamine dodecylbenzenesulfonate.

- Suitable amphoteric surfactants are, for example, alkylbetaines, alkylamidopropylbetaines, alkylsulfobetaines, alkyl glycinate,
- 25 alkyl carboxyglycinates, alkyl amphoacetates or -propionates, alkyl amphodiacetates or -dipropionates.

- For example, cocodimethylsulfopropylbetaine, laurylbetaine, cocamidopropylbetaine or sodium cocamphopropionate can be used.
- 30

- Suitable nonionic surfactants are, for example, the reaction products of aliphatic alcohols or alkylphenols having 6 to 20 carbon atoms in the alkyl chain, which may be linear or branched, with ethylene oxide and/or propylene oxide. The amount of
- 35 alkylene oxide is about 6 to 60 mol per mole of alcohol. Also suitable are alkylamine oxides, mono- or dialkyl alkanolamides, fatty acid esters of polyethylene glycols, ethoxylated fatty acid amides, alkyl polyglycosides or sorbitan ether esters.

- 40 In addition, the washing, shower and bath preparations can comprise customary cationic surfactants, such as, for example, quaternary ammonium compounds, for example cetyltrimethylammonium chloride.

- 45 In addition, further customary cationic polymers can also be used, such as, for example, copolymers of acrylamide and dimethyldiallylammonium chloride (Polyquaternium-7), cationic

cellulose derivatives (Polyquaternium-4, -10), guar hydroxypropyltrimethylammonium chloride (INCI: Hydroxypropyl Guar Hydroxypropyltrimonium Chloride), copolymers of N-vinylpyrrolidone and quaternized N-vinylimidazole

- 5 (Polyquaternium-16, -44, -46), copolymers of N-vinylpyrrolidone/dimethylaminoethyl methacrylate, quaternized with diethyl sulfate (Polyquaternium-11) and others.

- In addition, the washing and shower gel formulations and bath
10 preparations can comprise thickeners, such as, for example, sodium chloride, PEG-55, propylene glycol oleate, PEG-120 methyl glucose dioleate and others, and preservatives, further active ingredients and auxiliaries and water.

- 15 Hair cosmetic preparations include, in particular styling agents and/or conditioning agents in hair cosmetic preparations, such as hair treatments, hair mousses, (hair) gels or hair sprays, hair lotions, hair rinses, hair shampoos, hair emulsions, split-end fluids, neutralizing agents for permanent waves, hair colorants
20 and bleaches, hot-oil treatment preparations, conditioners, setting lotions or hair sprays. Depending on the field of use, the hair cosmetic preparations can be applied in the form of an (aerosol) spray, (aerosol) mousse, gel, gelspray, cream, lotion or wax.

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The hair cosmetic formulations according to the invention comprise, in a preferred embodiment,

- a) 0.05 to 20% by weight of the polymer according to the
30 invention
- b) 20 to 99.95% by weight of water and/or alcohol
- c) 0 to 79.5 % by weight of further constituents

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Alcohol is understood as meaning all alcohols customary in cosmetics, e.g. ethanol, isopropanol, n-propanol.

- Further constituents are understood as meaning the additives
40 customary in cosmetics, for example propellants, defoamers, interface-active compounds, i.e. surfactants, emulsifiers, foaming agents and solubilizers. The interface-active compounds used may be anionic, cationic, amphoteric or neutral. Further customary constituents may also be, for example, preservatives,
45 perfume oils, opacifiers, active ingredients, UV filters, care substances, such as panthenol, collagen, vitamins, protein hydrolyzates, alpha- and beta-hydroxycarboxylic acids,

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stabilizers, pH regulators, dyes, viscosity regulators, gelling agents, dyes, salts, humectants, refatting agents, complexing agents and further customary additives.

- 5 In addition, these include all styling and conditioning polymers known in cosmetics which can be used in combination with the polymers according to the invention if very specific properties are to be set.
- 10 Suitable conventional hair cosmetic polymers are, for example, anionic polymers. Such anionic polymers are homo- and copolymers of acrylic acid and methacrylic acid or salts thereof, copolymers of acrylic acid and acrylamide and salts thereof; sodium salts of polyhydroxycarboxylic acids, water-soluble or water-dispersible
- 15 polyesters, polyurethanes (Luviset® P.U.R.) and polyureas. Particularly suitable polymers are copolymers of t-butyl acrylate, ethyl acrylate, methacrylic acid (e.g. Luvimer® 100P), copolymers of N-tert-butylacrylamide, ethyl acrylate, acrylic acid (Ultrahold® 8, Strong), copolymers of vinyl acetate,
- 20 crotonic acid and optionally further vinyl esters (e.g. Luviset® grades), maleic anhydride copolymers, optionally reacted with alcohols, anionic polysiloxanes, e.g. carboxyfunctional copolymers of vinylpyrrolidone, t-butyl acrylate, methacrylic acid (e.g. Luviskol® VBM).
- 25 In addition, the group of polymers suitable for combining with the polymers according to the invention includes, for example, Balance® CR (National Starch; acrylate copolymer), Balance® 0/55 (National Starch; acrylate copolymer), Balance® 47 (National
- 30 Starch; octylacrylamide/acrylate/butylaminoethyl methacrylate copolymer), Aquaflex® FX 64 (ISP; isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer), Aquaflex® SF-40 (ISP / National Starch; VP/vinylcaprolactam/DMPA acrylate copolymer), Allianz® LT-120 (ISP / Rohm & Haas;
- 35 acrylate/C1-2 succinate/hydroxyacrylate copolymer), Aquarez® HS (Eastman; polyester-1), Diaformer® Z-400 (Clariant; methacryloylethylbetaine/methacrylate copolymer), Diaformer® Z-711 (Clariant; methacryloylethyl N-oxide/methacrylate copolymer), Diaformer® Z-712 (Clariant; methacryloylethyl
- 40 N-oxide/methacrylate copolymer), Omnirez® 2000 (ISP; monoethyl ester of poly(methyl vinyl ether/maleic acid in ethanol), Amphomer® HC (National Starch; acrylate/octylacrylamide copolymer), Amphomer® 28-4910 (National Starch; octylacrylamide/acrylate/butylaminoethyl methacrylate copolymer),
- 45 Advantage® HC 37 (ISP; terpolymer of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylate), Acudyne® 258 (Rohm & Haas; acrylate/hydroxy ester

acrylate copolymer), Luviset[®] PUR (BASF, polyurethane-1), Luviflex[®] Silk (BASF), Eastman[®] AQ48 (Eastman).

5 Very particularly preferred anionic polymers are acrylates with an acid number greater than or equal to 120 and copolymers of t-butyl acrylate, ethyl acrylate, methacrylic acid.

Further suitable hair cosmetic polymers are cationic polymers with the INCI name Polyquaternium, e.g. copolymers
 10 of vinylpyrrolidone/N-vinylimidazolium salts (Luviquat[®] FC, Luviquat[®] HM, Luviquat[®] MS, Luviquat[®] Care), copolymers of N-vinylpyrrolidone/dimethylaminoethyl methacrylate, quaternized with diethyl sulfate (Luviquat[®] PQ 11), copolymers of N-vinylcaprolactam N-vinylpyrrolidone/N-vinylimidazolium salts
 15 (Luviquat[®] Hold); cationic cellulose derivatives (Polyquaternium-4 and -10), acrylamide copolymers (Polyquaternium-7).

In addition, cationic guar derivatives, such as guar
 20 hydroxypropyltrimonium chloride (INCI), can be used.

Further suitable hair cosmetic polymers are also neutral polymers, such as polyvinylpyrrolidones, copolymers of N-vinylpyrrolidone and vinyl acetate and/or vinyl propionate,
 25 polysiloxanes, polyvinylcaprolactam and copolymers with N-vinylpyrrolidone, polyethyleneimines and salts thereof, polyvinylamines and salts thereof, cellulose derivatives, polyaspartic acid salts and derivatives.

30 To set certain properties, the preparations can additionally also comprise conditioning substances based on silicone compounds. Suitable silicone compounds are, for example, polyalkylsiloxanes, polyarylsiloxanes, polyaryalkylsiloxanes, polyether siloxanes, silicone resins or Dimethicone Copolyols (CTFA) and
 35 aminofunctional silicone compounds such as Amodimethicone (CTFA).

The polymers according to the invention are suitable, in particular, as setting agents in hair styling preparations, in particular hair sprays (aerosol sprays and pump sprays without
 40 propellant gas) and hair mousses (aerosol mousses and pump mousses without propellant gas).

In a preferred embodiment, these preparations comprise

- 45 a) 0.1 to 10% by weight of the polymer according to the invention
- b) 20 to 99.9% by weight of water and/or alcohol

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- c) 0 to 70% by weight of a propellant
- d) 0 to 20% by weight of further constituents.

Propellants are the propellants customarily used for hair sprays
 5 or aerosol mousses. Preference is given to mixtures of propane/butane, pentane, dimethyl ether, 1,1-difluoroethane (HFC-152 a), carbon dioxide, nitrogen or compressed air.

A formulation for aerosol hair mousses preferred according to the
 10 invention comprises

- a) 0.1 to 10% by weight of the polymer according to the invention
- b) 55 to 99.8% by weight of water and/or alcohol
- 15 c) 5 to 20% by weight of a propellant
- d) 0.1 to 5% by weight of an emulsifier
- e) 0 to 10% by weight of further constituents

Emulsifiers which can be used are all emulsifiers customarily
 20 used in hair mousses. Suitable emulsifiers may be nonionic, cationic or anionic or amphoteric.

Examples of nonionic emulsifiers (INCI nomenclature) are laureths, e.g. laureth-4; ceteths, e.g. ceteth-1, polyethylene
 25 glycol cetyl ether; cetearths, e.g. cetearth-25, polyglycol fatty acid glycerides, hydroxylated lecithin, lactyl esters of fatty acids, alkyl polyglycosides.

Examples of cationic emulsifiers are cetyldimethyl-2-
 30 hydroxyethylammonium dihydrogenphosphate, cetyltrimonium chloride, cetyltrimonium bromide, cocotrimonium methylsulfate, Quaternium-1 to x (INCI).

Anionic emulsifiers can, for example, be chosen from the group of
 35 alkylsulfates, alkyl ether sulfates, alkylsulfonates, alkylarylsulfonates, alkylsuccinates, alkylsulfosuccinates, N-alkoyl sarcosinates, acyl taurates, acyl isethionates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, alpha-olefinsulfonates, in particular the alkali metal and
 40 alkaline earth metal salts, e.g. sodium, potassium, magnesium, calcium, and ammonium and triethanolamine salts. The alkyl ether sulfates, alkyl ether phosphates and alkyl ether carboxylates can have between 1 and 10 ethylene oxide or propylene oxide units, preferably 1 to 3 ethylene oxide units, in the molecule.

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A preparation suitable according to the invention for styling gels can, for example, have the following composition:

- 5 a) 0.1 to 10% by weight of the polymer according to the invention
 - b) 60 to 99.85% by weight of water and/or alcohol
 - c) 0.05 to 10 % by weight of a gelling agent
 - d) 0 to 20% by weight of further constituents
- 10 Gelling agents which can be used are all gelling agents customary in cosmetics. These include slightly crosslinked polyacrylic acid, for example Carbomer (INCI), cellulose derivatives, e.g. hydroxypropylcellulose, hydroxyethylcellulose, cationically modified celluloses, polysaccharides, e.g. xanthum gum,
- 15 caprylic/capric triglycerides, sodium acrylates copolymer, Polyquaternium-32 (and) Paraffinum Liquidum (INCI), Sodium Acrylates Copolymer (and) Paraffinum Liquidum (and) PPG-1 Trideceth-6, Acrylamidopropyl Trimonium Chloride/Acrylamide Copolymer, Steareth-10 Allyl Ether Acrylates Copolymer,
- 20 Polyquaternium-37 (and) Paraffinum Liquidum (and) PPG-1 Trideceth-6, Polyquaternium 37 (and) Propylene Glycol Dicaprate Dicaprylate (and) PPG-1 Trideceth-6, Polyquaternium-7, Polyquaternium-44.
- 25 The polymers according to the invention can also be used in shampoo formulations as setting and/or conditioning agents. Suitable conditioning agents are, in particular, polymers with a cationic charge. Preferred shampoo formulations comprise
- 30 a) 0.05 to 10% by weight of the polymer according to the invention
- b) 25 to 94.95% by weight of water
- c) 5 - 50% by weight of surfactants
- d) 0 - 5% by weight of a further conditioning agent
- 35 e) 0 - 10% by weight of further cosmetic constituents

All anionic, neutral, amphoteric or cationic surfactants customarily used in shampoos can be used in the shampoo formulations.

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- Suitable anionic surfactants are, for example, alkyl sulfates, alkyl ether sulfates, alkylsulfonates, alkylarylsulfonates, alkyl succinates, alkylsulfosuccinates, N-alkoylsarcosinates, acyl taurates, acyl isethionates, alkyl phosphates, alkyl ether
- 45 phosphates, alkyl ether carboxylates, alpha-olefinsulfonates, in particular the alkali metal and alkaline earth metal salts, e.g. sodium, potassium, magnesium, calcium, and ammonium and

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triethanolamine salts. The alkyl ether sulfates, alkyl ether phosphates and alkyl ether carboxylates can have between 1 and 10 ethylene oxide or propylene oxide units, preferably 1 to 3 ethylene oxide units in the molecule.

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Suitable are, for example, sodium lauryl sulfate, ammonium lauryl sulfate, sodium lauryl ether sulfate, ammonium lauryl ether sulfate, sodium lauroyl sarcosinate, sodium oleyl succinate, ammonium lauryl sulfosuccinate, sodium dodecylbenzenesulfonate,
10 triethanolamine dodecylbenzenesulfonate.

Suitable amphoteric surfactants are, for example, alkylbetaines, alkylamidopropylbetaines, alkylsulfobetaines, alkyl glycinate, alkyl carboxyglycinates, alkyl amphotacetates or propionates,
15 alkyl amphodiacetates or dipropionates.

For example, cocodimethylsulfopropylbetaine, laurylbetaine, cocamidopropylbetaine or sodium cocamphopropionate can be used.

20 Suitable nonionic surfactants are, for example, the reaction products of aliphatic alcohols or alkylphenols having 6 to 20 carbon atoms in the alkyl chain, which may be linear or branched, with ethylene oxide and/or propylene oxide. The amount of alkylene oxide is about 6 to 60 mol per mole of alcohol. In
25 addition, alkylamine oxides, mono- or dialkylalkanolamides, fatty acid esters of polyethylene glycols, alkyl polyglycosides or sorbitan ether esters are suitable.

In addition, the shampoo formulations can comprise customary
30 cationic surfactants, such as, for example, quaternary ammonium compounds, for example cetyltrimethylammonium chloride.

In the shampoo formulations, to achieve certain effects, it is possible to use customary conditioning agents in combination with
35 the polymers according to the invention. These include, for example, cationic polymers with the INCI name Polyquaternium, in particular copolymers of vinylpyrrolidone/N-vinylimidazolium salts (Luviquat® FC, Luviquat® HM, Luviquat® MS, Luviquat® Care), copolymers of N-vinylpyrrolidone/dimethylaminoethyl
40 methacrylate, quaternized with diethyl sulfate (Luviquat® PQ 11), copolymers of N-vinylcaprolactam/N-vinylpyrrolidone/N-vinylimidazolium salts (Luviquat® Hold); cationic cellulose derivatives (Polyquaternium-4 and -10), acrylamide copolymers
45 (Polyquaternium-7). It is also possible to use protein hydrolyzates, and conditioning substances based on silicone compounds, for example polyalkylsiloxanes, polyarylsiloxanes,

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polyarylsiloxanes, polyethersiloxanes or silicone resins. Further suitable silicone compounds are Dimethicone Copolyols (CTFA) and aminofunctional silicone compounds, such as Amodimethicone (CTFA). In addition, cationic guar derivatives, 5 such as guar hydroxypropyltrimonium chloride (INCI) can be used.

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Table 2

Feed	X TAA Monomer (d)	Y MCOH Monomer (e)	Y PE(MC) ₄ Monomer (e)	k value 5 % NaCl solution	Solids content (%)	Tel Quel viscosity (mPas)	Reduction in combing force			
							Wet		Dry	
						(grade)	(%)	(grade)	(%)	
1	0.75	0.3	-	73.4	10	1-2	53%	1-2	72%	
2	0.75	0.3	-	77.8	12	1-2	51%	1-2	80%	
3	0.75	-	0.3	88.7	10	1-2	49%	1-2	83%	
C1	0.75	-	-	n.m.	12	1-2	52%	1-2	74%	
C2	-	0.3	-	24	13	2-	13%	2+	34%	
C3	0.75	-	-	83	7	1-2	50%	1-2	75%	

Abbreviations used (% by weight, in each case based on the total amount of monomer)

TAA = triallylamine (% by weight)

MCOH = mercaptoethanol (% by weight)

PE(MC)₄ = pentaerythritol tetramercaptoacetate (% by weight)

n.m. = not measurable due to the excessive amount of gel particles in the solution

The viscosity was determined using a Brookfield viscosimeter with spindle 4, 12 rpm at 25°C.

Examples

A: Preparation of polymers 1 to 3

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85.9 g of N-vinylpyrrolidone, 47.7 g of 3-methyl-1-vinylimidazolium methylsulfate (45% in water), X g of triallylamine (amount in Table 1) Y g of regulator (amount and regulator in Table 1) and varying amounts of water (750 to 920 g depending on the solids content; solids content data in Table 1) were initially introduced into a stirred apparatus and heated to 65°C in a stream of nitrogen with stirring. Then 25 g of a feed consisting of 1.6 g of 2,2'-azobis(2-amidinopropane) dihydrochloride in 65 g of water were metered in over 3 hours.

15 When the metered addition was complete, the mixture was stirred for a further hour at 65°C. The polymerization temperature was then increased to 70°C, and the remaining 2,2'-azobis(2-amidinopropane) dihydrochloride feed was added over a further hour. At the end of this metered addition, the mixture 20 was stirred for a further 2 hours.

This gave colorless polymer solutions with varying solids contents and viscosity (data in Table 2).

25 The comparison experiments were carried out accordingly with the components specified in Table 1.

B: Comparison of the properties of the polymers according to the invention with the polymers of the comparative examples

30

For the performance investigation, the polymers were used in a surfactant solution formulation having the following composition:

40.0%	of Texapon NSO (sodium laureth sulfate solution 28%; Cognis)
10.0%	of Tego-Betaine L7 (cocamidopropylbetaine solution 30%; Goldschmidt)
0.5%	of polymer (solids content) ad 100% of water

40 Determination of the combability

The following instructions describe the procedure for determining the wet and dry combability of hair following treatment with conditioning agents. All measurements were carried out in a 45 climatically controlled room at 65% relative humidity and 21°C.

Instruments used

Wet combability: Frank tensile/force tester
Dry combability: Diastron force measuring system
Digital balance: (top-pan balance)

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Hair:

a) European, bleached: hair tresses from Wernesgrün
(bleaching see below)

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b) Asiatic, untreated: hair tresses from Wernesgrün with split
ends

The following tests were carried out:

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- Wet combability following application of shampoo on European,
bleached hair
- Dry combability following application of shampoo on Asiatic
hair

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Pretreatment/cleansing of the hair:

Prior to the first use, the Asiatic hair tresses were cleansed in
25 a solvent mixture (ethanol/isopropanol/acetone/water 1:1:1:1)
until the hair appeared clean in the dry state (i.e. no longer
stuck together). The hair was then washed with sodium lauryl
ether sulfate.

30 The European hair was then treated with a bleaching paste (7.00 g
of ammonium carbonate, 8.00 g of calcium carbonate, 0.50 g of
Aerosil 200, 9.80 g of hydrogen peroxide (30% strength), 9.80 g
of demineralized water). The hair tresses were completely
immersed into the bleaching paste to ensure extensive wetting of
35 the entire surface of the hair. The tresses were then wiped
between the fingers in order to remove excess bleaching paste.
The contact time of the remaining bleach on the hair is matched
to the degree of damage required, and is generally 15 to 30
minutes, but can vary depending on the quality of the hair. The
40 bleached hair tresses were then thoroughly rinsed under running
tap water (2 minutes) and washed with sodium lauryl ether
sulfate. The hair was then dipped briefly into an aqueous acidic
solution (e.g. citric acid) because of so-called insidious
bleaching, and then rinsed with tap water.

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Applications:

The hair tress is dipped for 1 minute into the surfactant formulation to be tested, shampooed for 1 minute and then rinsed
5 for 1 minute under running drinking water (hand-hot).

I) Wet combability

Determination of the blank value for wet combability: the washed
10 hair was dried overnight in a climatically controlled room. Prior to measurement, it was shampooed twice with Texapon NSO for a total of 1 minute and rinsed for 1 minute so that it is definitely wet, i.e. swollen. Prior to the start of the measurement, the tress was precombed until knots were no longer
15 present in the hair and thus a constant application of force is necessary for the repeated measurement combing. The tress was then fixed to a support and combed using the finely-toothed side of the comb into the finely-toothed side of the test comb. The hair was inserted into the test comb for each measurement
20 uniformly and without tension. The measurement was started and evaluated by means of software (EGRANUDO program, Frank). The individual measurement was repeated 5 to 10 times. The calculated average value was noted.

25 Determination of the measurement value for wet combability: following the determination of the blank value, the hair was treated depending on the desired application. The combing force is measured analogously to the blank-value determination.

30 Evaluation:

Reduction in combing force wet [%] = $100 - (\text{measurement value} \times 100 / \text{blank value})$

35 II) Dry combability

Determination of the blank value for dry combability: the washed hair was dried overnight in a climatically controlled room. Prior to the start of the measurement, the tress was precombed until
40 knots were no longer present in the hair and thus a constant application of force is necessary for repeated measurement combing. The tress was then fixed to a support and combed into the finely-toothed side of the test comb. The hair was inserted into the test comb for each measurement uniformly and without
45 tension. The measurement was started and evaluated by means of software (mtt-win, DIASTRON). The individual measurement was

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repeated 5 to 10 times. The calculated average value was noted together with the standard deviation.

Determination of the measurement value for dry combability:

- 5 following the determination of the blank value, the hair was treated according to the desired application and dried overnight. The combing force was measured analogously to the blank-value determination. Evaluation:

- 10 Decreasing combing force dry [%] = $100 - (\text{measurement value} \times 100 / \text{blank value})$

The results are summarized in Table 2.

- The polymers to be used according to the invention (Examples 1 to 15 3) exhibit good performance properties and can be prepared with high solids contents.

- In contrast to this, polymers which have been prepared without monomer (e) produce excessively high viscosities (C-1) or an 20 excessively low solids content (C-3). Polymers which have been prepared by polymerization in the presence of a regulator but without crosslinker (C-2) exhibit good viscosities, but are unsatisfactory with regard to their performance properties.
- 25 The polymers to be used according to the invention produce excellent results with regard to dry combability, but, in particular, to wet combability. A further advantage is that clear (washing) formulations are also possible with the polymer according to the invention.
- 30 A further advantage is that the polymers to be used according to the invention can be prepared with high solids contents.

Example 4

- 35 In a 1 l stirred apparatus, 400 ml of water, 50 g of N-vinylpyrrolidone and 50 g of dimethyldiallylammonium chloride solution (65% strength) were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at
- 40 200 revolutions/min. At this temperature, a first feed comprising 2 g of 2,2'-azobis(2-methylbutyronitrile) and 0.3 g of mercaptoethanol in 30 g of isopropanol and, in parallel, a second feed comprising 2 g of divinylethyleneurea in 30 ml of isopropanol was added over the course of 1.5 hours. The reaction
- 45 mixture was stirred for a further 3 hours at this temperature.

The isopropyl alcohol was then removed from the reaction mixture by means of steam distillation.

Example 5

5

In a 1 l stirred apparatus, 400 ml of water, 100 g of dimethyldiallylammonium chloride solution (65% strength) were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at 200 revolutions/min. At this temperature, a
10 first feed comprising 2 g of 2,2'-azobis(2-methylbutyronitrile) and 2.5 g of mercaptoethanol in 30 g of isopropanol and, in parallel, a second feed comprising 8 g of N,N'-divinylethyleneurea in 70 ml of isopropanol was added over the course of 1.9 hours. The reaction mixture was stirred for a
15 further 2 hours at this temperature. The isopropyl alcohol was then removed from the reaction mixture by means of steam distillation.

Example 6

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In a 1 l stirred apparatus, 400 ml of water were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at 200 revolutions/min. At this temperature, a first feed comprising 2 g of 2,2'-azobis(2-methylbutyronitrile) and 2 g of mercaptoethanol
25 in 30 g of isopropanol and, in parallel, a second feed comprising 6 g of methylenebisacrylamide, 50 g of N-vinylpyrrolidone and 50 g of 2-methyl-1-vinylimidazolium methylsulfate solution (45% strength) was added over the course of 2 hours. The reaction mixture was stirred for a further 3.5 hours at this temperature.
30 The isopropyl alcohol was then removed from the reaction mixture by means of steam distillation.

Example 7

35 In a 1 l stirred apparatus, 400 ml of water, 50 g of N-vinylpyrrolidone and 50 g of 2-methyl-1-vinylimidazolium methylsulfate solution (45% strength) were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at 200 revolutions/min. At this temperature, a first feed comprising 2 g
40 of 2,2'-azobis(2-methylbutyronitrile) and 2 g of mercaptoethanol in 30 g of isopropanol and, in parallel, a second feed comprising 4 g of divinylethyleneurea in 30 ml of isopropanol was added over the course of 1.75 hours. The reaction mixture was stirred for a further 3.5 hours at this temperature. The isopropyl alcohol was
45 then removed from the reaction mixture by means of steam distillation.

Example 8

In a 1 l stirred apparatus, 400 ml of water, 50 g of N-vinylpyrrolidone and 50 g of N,N-dimethylaminoethylmethacrylate methyl chloride salt solution (50% strength) were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at 200 revolutions/min. At this temperature, a first feed comprising 2 g of 2,2'-azobis(2-methylbutyronitrile) and 5 g of mercaptoethanol in 30 g of isopropanol and, in parallel, a second feed comprising 10 g of divinylethyleneurea in 70 ml of isopropanol was added over the course of 1.85 hours. The reaction mixture was stirred for a further 3.5 hours at this temperature. The isopropyl alcohol was then removed from the reaction mixture by means of steam distillation.

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Example 9

In a 1 l stirred apparatus, 400 ml of water and 100 g of N,N-dimethylaminoethyl methacrylate methyl chloride salt solution (50% strength) were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at 200 revolutions/min. At this temperature, a first feed comprising 2 g of 2,2'-azobis(2-amidinopropane) dihydrochloride and 5 g of mercaptoethanol in 30 g of water and, in parallel, a second feed comprising 8 g of triethylene glycol diacrylate in 50 ml of water was added over the course of 2 hours. The reaction mixture was then stirred for a further 3 hours at this temperature. The reaction mixture was then subjected to steam distillation.

30 Example 10

In a 1 l stirred apparatus, 400 ml of water and 50 g of vinylpyrrolidone and 50 g of N,N-dimethylaminoethyl methacrylate methyl chloride salt solution (50% strength) were heated to 80°C in a stream of nitrogen with stirring using an anchor stirrer at 200 revolutions/min. At this temperature, a first feed comprising 1 g of 2,2'-azobis(2-methylbutyronitrile) and 1 g of mercaptoethanol in 30 g of isopropanol and, in parallel, a second feed comprising 2 g of divinylethyleneurea in 30 ml of isopropanol was added over the course of 1.5 hours. The reaction mixture was stirred for a further 3 hours at this temperature. The isopropanol was then removed from the reaction mixture by means of steam distillation.

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Example 11 - Clear conditioner shampoo

	%	Ingredient	INCI
	15.00	Tego Betaine L 7	Cocamidopropylbetaine
	10.00	Amphotensid GB 2009	Disodium cocoamphodiacetate
5	5.00	Cremophor PS 20	Polysorbate 20
	5.00	Plantacare 2000	Decyl glucoside
	3.00	Stepan PEG 6000 DS	PEG-150 distearate
	q.s.	Perfume	
	q.s.	Preservative	
10	q.s.	Citric acid	
	0.1-1.0	Active substance of conditioner polymer as in Example 1	
	2.00	Rewopal LA 3	Laureth-3
	ad 100	Water, demineralized	Aqua dem.

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Example 12 - Conditioner shampoo

	%	Ingredient	INCI
	30.00	Texapon NSO	Sodium laureth sulfate
	6.00	Dehyton G	Sodium cocoamphoacetate
20	6.00	Dehyton K	Cocamidopropylbetaine
	3.00	Euperlan PK 771	Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
	0.1-1.0	Active substance of conditioner polymer as in Example 1	
25	2.00	Dimethicone	
	q.s.	Perfume	
	q.s.	Preservative	
	q.s.	Citric acid	
30	1.00	Sodium chloride	
	ad 100	Water, demineralized	Aqua dem.

Example 13 - Conditioner shampoo

	%	Ingredient	INCI
35	30.00	Texapon NSO	Sodium laureth sulfate
	6.00	Dehyton G	Sodium cocoamphoacetate
	6.00	Dehyton K	Cocamidopropylbetaine
	3.00	Euperlan PK 771	Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
40	0.1-1.0	Active substance of conditioner polymer as in Example 2	
	2.00	Amidodimethicone	
	q.s.	Perfume	
45	q.s.	Preservative	
	q.s.	Citric acid	
	1.00	Sodium chloride	

45

ad 100	Water, demineralized	Aqua dem.
Example 14 - Conditioner shampoo		
	%	Ingredient
5	40.00	Texapon NSO
	10.00	Dehyton K
	3.00	Euperlan PK 771
		Sodium laureth sulfate
		Cocamidopropylbetaine
		Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
10	0.1-1.0	Active substance of conditioner polymer as in Example 2
	2.00	Dow Corning 3052
	q.s.	Perfume
	q.s.	Preservative
15	q.s.	Citric acid
	2.00	Cocamido DEA
ad 100	Water, demineralized	Aqua dem.
Example 15 - Conditioner Shampoo		
20	%	Ingredient
	30.00	Texapon NSO
	6.00	Dehyton G
	6.00	Dehyton K
	3.00	Euperlan PK 771
25		Sodium laureth sulfate
		Sodium cocoamphoacetate
		Cocamidopropylbetaine
		Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
	0.1-1.0	Active substance of conditioner polymer as in Example 2
	2.00	Dimethicone
30	q.s.	Perfume
	q.s.	Preservative
	q.s.	Citric acid
	2.00	Cocamido DEA
ad 100	Water, demineralized	Aqua dem.
35	Example 16 - Anti-dandruff shampoo	
	%	Ingredient
	40.00	Texapon NSO
	10.00	Tego Betain L 7
40	10.00	Rewopol SB FA 30
		Disodium laureth sulfo- succinate
	2.50	Euperlan PK 771
		Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
45	0.1-1.0	Active substance of conditioner polymer as in Example 3
	0.50	Crinipan AD
		Climbazole

	q.s.	Perfume	
	q.s.	Preservative	
	q.s.	Citric acid	
	0.50	Sodium chloride	
5	ad 100	Water, demineralized	Aqua dem.

Example 17 - Shampoo

	%	Ingredient	INCI
	25.00	Sodium laureth sulfate	
10	5.00	Cocamidopropylbetaine	
	2.50	Euperlan PK 771	Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
	0.1-1.0	Active substance of conditioner polymer as in Example 3	
15	2.0	Cocamido DEA	
	q.s.	Perfume	
	q.s.	Preservative	
	ad 100	Water, demineralized	Aqua dem.

20

Example 18 - Shampoo

	%	Ingredient	INCI
	20.00	Ammonium laureth sulfate	
	15.00	Ammonium lauryl sulfate	
25	5.00	Cocamidopropylbetaine	
	2.50	Euperlan PK 771	Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
	0.1-1.0	Active substance of conditioner polymer as in Example 3	
30	q.s.	Perfume	
	q.s.	Preservative	
	0.50	Sodium chloride	
	ad 100	Water, demineralized	Aqua dem.

35

Example 19 - Shampoo

	%	Ingredient	INCI
	20.00	Sodium laureth sulfate	
	15.00	Sodium lauryl sulfate	
40	5.00	Cocamidopropylbetaine	
	2.50	Euperlan PK 771	Sodium laureth sulfate, glycol distearate, cocamide MEA, laureth-10
	0.1-1.0	Active substance of conditioner polymer as in Example 2	
45	q.s.	Perfume	
	q.s.	Preservative	

0.50 Sodium chloride
ad 100 Water, demineralized Aqua dem.

Example 20 - Clear shower gel

5	%	Ingredient	INCI
	40.00	Texapon NSO	Sodium laureth sulfate
	5.00	Plantacare 2000	Decyl glucoside
	5.00	Tego Betain L 7	Cocamidopropylbetaine
	0.1-1.0	Active substance of conditioner polymer as in Example 2	
10	1.00	D-Panthenol USP	Panthenol
	q.s.	Perfume	
	q.s.	Preservative	
	q.s.	Citric acid	
15	2.00	Sodium chloride	
	ad 100	Water, demineralized	Aqua dem.

Example 21 - Shampoo

	%	Ingredient	INCI
20	12.00	Texapon N 70	Sodium laureth sulfate
	1.50	Plantacare 2000	Decyl glucoside
	2.50	Dehyton PK 45	Cocamidopropylbetaine
	5.00	Lamesoft PO 65	Cocoglucoside glyceryl oleate
	2.00	Euperlan PK 771	Sodium laureth sulfate,
25			glycol distearate, cocamide
			MEA, Laureth-10
	0.1-1.0	Active substance of conditioner polymer as in Example 1	
	q.s.	Preservative	
30	q.s.	Sicovit Sunset Yellow 85 E 110	Sunset Yellow C.I. 15 985
	q.s.	Perfume	
	1.00	Sodium chloride	
	ad 100	Water, demineralized	

35

Example 22 - Shampoo

	%	Ingredient	INCI
	12.00	Texapon N 70	Sodium laureth sulfate
	1.50	Plantacare 2000	Decyl glucoside
40	2.50	Dehyton PK 45	Cocamidopropylbetaine
	5.00	Lamesoft PO 65	Cocoglucoside glyceryl oleate
	2.00	Euperlan PK 771	Sodium laureth sulfate,
			glycol distearate, cocamide
			MEA, Laureth-10
45	0.1-1.0	Active substance of conditioner polymer as in Example 1	
	q.s.	Preservative	

48

q.s.	Sicovit Sunset	Sunset Yellow C.I. 15 985
		Yellow 85 E 110
q.s.	Perfume	
1.00	Sodium chloride	
5 ad 100	Water, demineralized	

10

15

20

25

30

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